Joint Russian and Bulgarian Academies of Sciences Data Base

of Intermolecular Potentials and Diffusion Coefficients

of the Components of the CVD-Processes in Microelectronics[1]

L.Fokin[2,4], V.Popov[2], A. Kalashnikov[2], L. Zarkova[3], P. Pirgov[3], I. Petkov[3]

[2] Institute of High Temperatures Russian Academy of Sciences, Izhorskaya 13/19, Moscow 127412, Russia.

[3] Institute of Electronics Bulgarian Academy of Sciences, Tsarigradsko Chaussee, 72, Sofia 1784, Bulgaria.

[4] To whom correspondence should be addressed.

ABSTRACT

The goal of the data base (DB) "EPIDIF-JRB" is to promote the modelling of the gasphase transport processes in CVD-technologies in the microelectronics at first place. The transport properties (molecular diffusion coefficients, viscosity, thermal conductivity) of pure gases and gas mixtures in the temperature range 250÷2000 K and pressure < 0.1 MPa are calculated on the background of 1) Chapman-Enskog method in binary collision approximation; 2) three-parameter Lennard-Jones m-6 intermolecular potentials (IP) with 8<m<100 for interactions of atoms and quasi-spherical molecules and four-parameter m-6-3 Stockmayer IP for dipole molecules. Except IP parameters a_{ii}, a_{jj} and a_{ij} the DB supplies also their variance-covariance matrix. For the heavy globular molecules (such as CF_4, SiH_4, $Si(CH_3)_4$, WF_6 etc.) we consider the influence of the vibrational excitation on their effective size. In this case isotropic Lennard-Jones m-6 IP with temperature dependent parameters was defined . At present DB "EPIDIF-JRB" contents 40 species with an important impact on the Si gas-phase-epitaxy processes, and IP parameters for 820 (!) pair interactions, that allows to calculate tables of the viscosity for pure gases and gas mixtures with any k components (k<11) and to estimate their error as well. DB is open for users and partners.

KEY WORDS: CVD processes, database, diffusion coefficients, intermolecular potentials, silicon epitaxy, gas viscosity.

1.   INTRODUCTION

The processes of producing substances by means of the gas-phase transport of the components (chemical vapor deposition, CVD- processes) occupy an important place in contemporary material science. They are a part of the high technologies which allows us to control the purities and the structure of the crystal e.g. the material properties.

Such approach has been used to obtain many classes of substances: semiconductors of high purity (Si, Ga, GaAs, etc.); compounds of elements of different groups (I-II, III-V, etc.) which are creating Si-like structures; metals (Cu, Pt, W, Mo, Ti, Zr…); thin oxide films (SiO_2, Al_2O_3); carbides; nitrides; high temperature semiconductors such as $YBa_2Cu_3 O_7$. The number of such substances is many hundreds. For example in one of the first monographs on CVD the author mentioned 118 transported species [1]. Perhaps, their number is now ten times larger. Note that the number of the abstracts in *Chemical Abstr*acts for the first half of 1995 was about 2500.

One has to remember that each expected substance requires 2-3 transported agents (precursors) – organic or metallorganic substances. These precursors as a rule have to be dissolved in a medium of gases-carriers (H_2, He, N_2, etc.). Therefore, intermediate species could also appear in the gas-phase. These particles will participate in the mass transport process towards the substrate, and part of them will return back to the gas volume.

It is obvious that the modelling CVD-processes in semiconductor microelectronics in particular, requires a knowledge of the thermophysical properties of many thousands of substances. Therefore, the organization of the information- reference

supply of necessary data for the CVD processes calculation has became a task of world scale.

Presently existing CVD processes usually take place at temperatures $T=$ 500 to 1700 K and at pressures $p<$ 0.1 MPa. In these conditions the gas-phase thermodynamic properties are described by means of the perfect gases mixture model in the local equilibrium approximation, or taking into account the chemical reactions rates. At the same time, the transport processes of the impulse, mass and heat transport are considered in the approximation of binary like or unlike interactions between the gas species. In addition, the kinetic coefficients (viscosity , thermal conductivity , diffusion D and thermal diffusion coefficients are calculated on the background of the modern molecular theory of gases [2]. The intermolecular potentials (IP) are the backbone of this theory. This is why the calculations of the transport properties of the gas substances presented in CVD-processes demand creation of a database (DB) contaning: a) IP of like or unlike interactions between the main participating in CVD species; b) calculational procedures for defining the transport properties. The objectives of such DB are to raise the user's interest and to satisfy the requirements of the local and long-distance users by means of PC computation.

Our DB EPIDIF is mainly oriented to the modelling of the silicon gas-phase epitaxy. Additionally, the set of the components permits users to calculate the transport properties of the products of organic fuels combustion.

There already exist and function several different packages of computational programs for CVD processes calculations. One of them has been developed in SANDIA Laboratory (USA) [3]. A "CVD Simulation Software" has been promoted by PHOENICS [4]. To our knowledge, both these packages produce determined

evaluations of the properties. The advantages of DB EPIDIF is that it allows the user to estimate the uncertainties of the results. This opportunity is of a great importance for the sensitivity analysis.

2. THEORETICAL BACGROUND

2.1. Potentials of binary interactions between the particles

2.1.1. *Polar and unpolar molecules*

Instead of the wide spread spherically-symmetric Lennard-Jones (LJ) (12-6) potential we are using for atom and unpolar molecules interactions a generalized LJ (*m*-6) potential with three independent variable parameters: the equilibrium distance R_e , the potential well depth ε and the repulsive parameter *m*.

It can be written as

$$\frac{U(R,a)}{\varepsilon} = \frac{6}{m-6} x^m - \frac{m}{m-6} x^6, \tag{1}$$

where $x = Re/R$, R – the distance between two interacting particles and *a* – the vector of the parameters. The choice of this class of potentials is motivated (a) by the specificity of the CVD processes for semiconductors which are very often taking place in the surrounding of light gases-carriers, such as H_2, He; and (b) by the possible participation in the processes of heavy globular molecules such as $SiCl_4$, MoF_6, WF_6 etc. It is well known that $m = 8$-9 for the molecular hydrogen while for WF_6 it is >15. This contradiction can not be resolved in the frame of LJ (12-6) IP. Moreover, at some defined conditions intermediate products of reactions (such as $SiH_4 \rightarrow SiH_3, SiH_2,$ SiH) could appear in the gas space. These particles do not exist as a stable substances at normal conditions. It can be expected that the estimation of the IP parameters of these components could be made using some methods developed for LJ (12-6) potentials.

The fact that we have already defined IP is not enough for modelling CVD-processes. To carry out the transport coefficient's properties calculation one needs also sets of collision integrals (CI) $Q^{(l,s)}(T)$ for each type of potentials. For LJ (*m*-6) we have approximated [5,6] in a wide range of reduced temperatures $T* = T / \varepsilon$ 0.4-200 and *m* = 8-∞ the best available tables [7,8] $Q^{(1,1)}(T*),Q^{(1,2)}(T*),Q^{(2,2)}(T*)$ by means of a parameterized expressions $\omega^{(l,s)}(T*, m, a)$. Simultaneous approximation $Q^{(l,s)}(T*)$ and $Q^{(l,s+1)}(T*)$ insured the internal self-consistency of CI. The collisional integrals for the Sutherland potential have been included for the sake of the correct approximation at $1/m \rightarrow 0$.

Usually, between the initial substances of the CVD processes and/or in the reaction's products there are also polar molecules, such as $SiHCl_3$, HCl, HF and H_2O molecules with large dipole moments . The interactions between like and unlike polar molecules are defined by means of a generalized Stockmayer potential with a spherically symmetric kernel e.g. LJ (*m*-6)

$$\langle Q^{(l,s)}(T) \rangle = Q^{(l,s)}(T)(LJ(m-6)) + A_l \delta^2 / T *, \qquad (2)$$

where the reduced dipole moment is $\delta = \mu_1 \mu_2(T) /(d^3 \varepsilon)$. The parameters A_1= 0.19 and A_2= 0.20 are taken from the calculations made earlier for LJ (12-6) by Brokaw [9]). The relation (2) was used to calculate the averaged with respect to the orientation CI in the DB EPIDIF. It was assumed that for polar-unpolar molecules' interactions the corrections bound to the dipole – induced dipole terms of IP could be neglected.

2.1.2. *Quasi-spherically symmetric (globular) molecules*

In the consideration of the interactions in pure gases and mixtures one has to have in mind the fact that many of the molecules (particularly, the large ones) have low

normal vibrational frequencies (in order of about 100-200 cm^{-1}). As a result, at temperatures 300–400 K and higher these molecules are vibrationally excited. Therefore, the effective inter-atomic distances in the molecules are increasing reflecting the temperature, and this leads to the corresponding change of IP. At a given temperature the gas of such molecules is considered as a mixture of different vibrationally excited states and ground state [10]. The interaction between each pair is described by a LJ (*m*-6) potential with different slightly increasing equilibrium distance. In first approximation we have an isotropic potential with temperature-dependent parameters (ITDP) [11] for calculation the properties of these gases.

A special procedure and computational codes have been developed in order to take into account this phenomena in DB. It consists of the following steps:

- calculation of the temperature dependence of the averaged over all excited states relative populations of the excited levels;

- defining the ITDP parameters $R_e^{eff}(T) = f(T)$, $\varepsilon^{eff}(T)$ and m minimizing the weighted sum of squared deviations between experimental and calculated properties data (for example, 2d virial and diffusion coefficients, viscosity η etc.). Here $f(T)$ is a correction obtained multiplying the forth variable parameter of IP, δ_1(enlargement of the molecule excited from the ground state to the first level) and the averaged relative population at the temperature T.

This approach has been successfully applied to the pure tetrahedral [11,12,13] (CF$_4$, SiF$_4$, CCl$_4$) and octahedral [11,14,15] (SF$_6$, UF$_6$, WF$_6$, MoF$_6$) gases, BF$_3$ [16] and some mixtures of them [12,17].

Further on, the achieved by means of ITDP tables (T) were re-approximated in the range 300-1500 K using three parameters IP LJ (m-6) (1). These parameters (m, ε and Re) are included in DB EPIDIF.

The problem arising when applying the procedure described above, is the lack of measured thermophysical properties for molecules with low vibrational frequencies. Usually, such experiments are carried out in a narrow temperature range (T<1000 K) and often with a not high accuracy.

2.2. Thermophysical properties

2.2.1. *Diffusion coefficients*

In the DB EPIDIF the binary diffusion coefficients of i,j components of the gas mixtures (at density p=1 atm) are calculated at given T:

- $[D_{ij}]_1$ in a first theory approximation [1], and

- $[D_{ij}]_2=[D_{ij}]_1(1+\ )$ – in a second theory approximation taking into account the slight (of about 2 %) influence of the sort of the constituents x. The correction $(1+\ )$ is calculated by means of the approximation [18] which includes only CI $Q^{(1,1)}$, $Q^{(1,2)}$, $Q^{(2,2)}$, the ratio of molecular weights M_1/M_2 and the mole fraction x of the heavy component. At x and M_1/M_2=1 D_{ij} is a self-diffusion coefficient.

It is up to the DB user's intention to determine also the coefficients of the generalized $D_{i\ gen}(T, x)$ or the multicomponent $D_i(T, x)$ diffusion of the i-species in the gas mixture with mole fractions x in the desirable variant [9].

2.2.2. *Viscosity*

For pure gases $\eta(T)$ is calculated by means of the well known expressions [2] in the second theory approximation.

The viscosity of a gas mixtures (the number of components $k<11$) instead as ratio of the determinants is calculated as a matrix product in the half as mach against the approximation [19]:

$$[\eta_{mix}(T,x)]_{1.5} = x^{tr} H^{-1} x,$$ (3)

where x is the mole fractions column-vector. The dimension of the matrix H as well as of the inverse one H^{-1} is given in a first approximation and is equal to $k \cdot k$ though it's h elements include the viscosity values $[\eta_{ii}]_2$, $[\eta_{ij}]_2$ and $[\eta_{jj}]_2$ in a second approximation. For example,

$$[h_{ij}]_{1.5} = -\frac{2x_i x_j}{[\eta_{ij}]_2} \frac{M_i M_j}{(M_i + M_j)^2} \left(\frac{5}{3A_{ij}^*} - 1\right), i \neq j.$$ (3a)

Here we have to keep in mind that the mixture's viscosity derivatives over the potential parameters required for the calculation of the confidential level are determined as

$$\frac{\partial(\eta_{mix})}{\partial a_p} = -x^{tr} H^{-1} H' H^{-1} x$$ (4)

where H' is a matrix of the element's derivatives dh/da_p [20].

2.2.3. *Thermal conductivity*

The calculation of the thermal conductivity for pure molecular gases includes terms which are proportional to the so called collision numbers $Z_{col}(T)$ ($Z_{rot}(T)$ or $Z_{vib}(T)$). There is a reserved room in the DB for such information although it is not available at present for the main part of the components considered. This is particularly true for interactions between unlike particles. The possibility to replace $Z_{col}(T)$ and $Z_{rot}(T)$ by corresponding combinations of the binary self-diffusion coefficients as suggested by Uribe [21] is discussed.

The calculation of the thermal conductivity of chemically reacting mixtures requires additional terms to take into account the heat's effects of the reactions. These depend on the numbers of factors which are too specific to be considered in the scope of our DB.

3. DATABASE FEATURES

The structure and algorithms for calculations described above shape the top of the thermophysical iceberg. It's "under water" background are publications reporting the input potential-dependent thermophysical properties data of gases and their mixtures; critical analysis of the experimental data; procedures for defining potential parameters and their error matrix; statistical analysis of the calculated data; and finally, using the DB by means of PC, marketing, management, and establishing connections with the users.

3.1. Considered objects

The data in the DB EPIDIF can be conditionally divided into two groups.

3.1.1. *Completely investigated molecules*

This group consists of pure gases with well measured properties in the temperature range of interest, such as Ar, Hg vapors, N_2, O_2, H_2, CO_2. For these gases the recognized by Russian GSSSD tables for $\eta(T)$ [22] have been used. These dependencies have been re-approximated by means of a LJ (m-6) potential (1). The corresponding potential parameters and the error matrix are given in the DB. The accuracy of the data measured for these gases , in particular for Ar and N_2, has reached an extremely high level due to the joint efforts put by thermophysists from different countries.

In this group we includealso the data of the steam as a typical representative of the polar molecular gases. A special procedure for proceeding these data by means of the Stokmayer potential has been introduced recently [23].

A special place in this first group is occupied by heavy globular molecules (for example, BF_3, CH_4, $SiCH_4$, $GeCH_4$, CF_4, SiF_4, GeF_4, $SiCl_4$, $GeCl_4$, SF_6, UF_6, WF_6, MoF_6, etc.). These data can be analyzed and proceeded by means of the ITDP approach. For some of them IP and corresponding thermophysical properties tables are produced in the Bulgarian Institute of Electronics during the last several years [11-17]. For others the available data are not enough, or do not exist.

3.1.2. *Partially investigated particles*

We reserve room for particles for which we are still not ready to supply data and/or to recommend the procedures for calculations. We keep studying them because they also have a substantial impact on the CVD-processes. Here belong for example, the polar chlorine and fluorine molecules, such as $SIHCl_3$; the atomic hydrogen-like components with interactions governed by some potential curves (H, C, N, O, Si); radicals of methane (CH_3, CH_2, CH), silane (SiH_3, SiH_2, SiH) or germane (GeH_3, GeH_2, GeH).

At present a research is undertaken in order to choose/create the appropriate procedures to enable us to define the IP in all these cases.

3.2. Interactions in mixtures of unlike molecules

Presently, for the multi-components ($k \geq 4$) mixtures are the binary interactions between like molecules though the unlike binary interactions are dominating. Usually, the last one are calculated by means of the empirical mixture rules for different physical properties, potential parameters or potentials.

In our DB there are two alternative possibilities: to use (a) the individual potential parameters of unlike molecules a_{ij}, or (b) the common combination rules of the sort of $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$. Recently a special procedure for simultaneous fit of different properties data of pure gases and binary mixtures has been developed [20]. It permits to restore simultaneously σ_{ii}, ε_{ii}, m_{ii}, σ_{ij}, ε_{ij}, m_{ij} ($i=1$, $j=2$) using LSM and to receive a variance-covariance matrix (VCM). This approach is applied in the DB to seven binary mixtures Ar-H_2, Ar-N_2, O_2-N_2, H_2O-CO_2, H_2O-N_2, H_2O-O_2, H_2-CO. Experimental D_{12}, η_{11}, η_{22} and η_{mix} data have been used to define for the first LJ(m-6) potential parameters and the corresponding VCM. Similar procedures for the binary mixtures of noble and some technically important gases have been reported by Kestin et al [18]. The shortcoming of these results is the lack of VCM.

Some results for the experimental N_2, O_2, N_2-O_2 data approximation by means of weighted LMS (number of points $n=203$; LMS sum $S=34.8$) are given in table I.

Table I. Parameters a_{ij} IP (1) and their rms[*] $\pm s_{ij}$

for three pairs N_2-N_2, N_2-O_2, and O_2-O_2[**].

a_{ij}	N_2-N_2	N_2-O_2	O_2-O_2
d_{ij}, A	3.645±0.015	3.509±0.033	3.425±0.022
ε_{ij}, K	98.28 ±2.77	110.75 ±6.80	115.35 ±4.65
m_{ij}	11.59 ±0.34	11.60 ±0.80	11.55 ±0.55

[*] rms — root mean square;

[**] if $m_{11}=m_{22}=m_{12}=12$, than $S=37.0$; if $a_{ij}=f(a_{11}, a_{22})$, than $S=37.9$.

For pure gases and gas mixtures Mason, Kestin and coautors are developed Corresponding-State-Principle. For example, in 1989 Bzhovski et al [24] calculated the

viscosity, diffusion coefficient and second virial coefficient of a great number of binary mixtures of noble and polyatomic gases. The results were absolutely acceptable with an exception for the mixtures SF_6 and CF_4. Later, the calculations were repeated by means of ITDP [25] for three mixtures SF_6-CF_4, SF_6-CH_4, and CF_4-CH_4. Then the deviations between experimental and calculated 2VC data have diminished 2 to 3 times and new potential parameters have been determined. Similarly, the mixtures of WF_6, UF_6 and MoF_6 thermophysical properties data have been calculated. We hope that this procedure could be profitable in some cases considered in the DB.

4.   STRUCTURE OF THE DB AND USER INTERFACE

The tool used when building the DB Borland C++ Builder.

The information about the potential parameters is included in a shape of a 3-dimensional matrix $C(3k,3k,6)$ where k is the number of the components, 6- number of the 2-dimensional matrix layers. Now we have k=40.

At this moment the DB EPIDIF works with the next gases: Ar, AsH_3, C, Cl_2, CO, CO_2, F_2, $Ga(CH_3)_3$, $GeBr_4$, $GeCl_4$, $GeCl_3F$, GeH_4, H, H_2, H_2O, HCl, He, HF, Hg, N, N_2, O, O_2, SF_6, Si, $SiBr_4$, $SiCl_4$, SiF_4, SiH, $SiHCl_3$, SiH_2, SiH_3, SiH_4, Si_2H_2, Si_2H_6, Si_3H_8, SiI_4, WF_6.

DB supplies the next opportunities:

-   to select a pair of molecules and to calculate at a given temperature T and mole fractions their D_{ii}, D_{ij} in 1st and 2nd approximation; η_{11}, η_{22}, η_{mix} together with the confidential error levels for all values;

-   to input any $k \leq 11$ mixture components and to calculate at a given T all binary diffusion coefficients and viscosity of gas mixture and estimated errors;

-   to check the input data and to upgrade it if necessary.

5. CONCLUSION

A database is designed in order to enable the programmers, the engineers and the researchers in the field of microelectronics, material and combustion sciences,   and everywhere where the mass, impulse or heat transport properties of molecular gases are present. It is friendly for users and helps them to get rapidly a reliable general picture of the processes of interactions in the case of interest.

The DB is open for upgrade and improvements. Our next future tasks are bound to the properties and potential of like and unlike particles interactions for pure polar molecules and radicals, and their mixtures with already investigated molecules.

6. AKNOWLEDGMENT

REFERENCES

1. H. Schafer, *Chemical Transport Reactions* (Acad. Press: NY, 1964).

2. J.H. Ferziger, H.G. Kaper, *Mathematical Theory of Transport Processes* (North-Holland Publ. Co., Amst. -L.,1972).

3. R.J. Kee, J. Warnatz, and J.A. Miller, *SANDIA Lab. Rt. SAND* 83-8209 (Albuquerque,1983).

4. H.I. Rosten, D.B. Spalding, *CHAM TR/100* (Wimbledon, 1987).

5. A.N. Kalashnikov, L.R. Fokin, *JIHT preprint 1-409* (JIHT, Moscow, 1997).

6. L.R. Fokin, A.N. Kalashnikov, *High Temperature* **37**: 49 (1999).

7. M. Klein, H.J.M. Hanley, F.J. Smith, and P. Holland, *NSRDS-NBS 47* (Gov. Print. Office, Wash.,1974).

8. M. Klein, F.J. Smith, *J. Res. NBS* **72A**: 359 (1968).

9. R.C. Reid, J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquids, 3d ed.* (McGraw-Hill, NY, 1987).

10. B. Stefanov, *J. Phys.B: At. Mol. Phys.* **25**: 4519 (1992).

11. L. Zarkova, *Mol. Phys.* **88**: 489 (1996).

12. L. Zarkova, P. Pirgov, and I. Petkov, *High Temp.-High Pressure* **29**: 365 (1997).

13. L. Zarkova, P. Pirgov, and I. Petkov, *J. Phys.B: At. Mol.Phys.* **31**: 805 (1998).

14. L. Zarkova, P. Pirgov, *ibid*, **28**: 4269 (1995).

15. L. Zarkova, P. Pirgov, *ibid*, **29**: 4441 (1996).

16. L. Zarkova, P. Pirgov, and G. Paeva, *ibid*, **32**: 1535 (1999).

17. L. Zarkova, I. Petkov, and P. Pirgov, *Bulg. J. Phys.* **25**: 134 (1998).

18. J. Kestin, K. Knierim, E.A. Mason, B. Najafi, S.T. Ro, and M. Waldman, *J. Phys. Chem.Ref. Data* **13**:229 (1984).

19. T.S. Storvick, E.A. Mason, *J. Chem. Phys.* **45**: 3752 (1966).

20. L.R. Fokin, N.A. Slavinskaya, *High Temperature* **25**: 40 (1987).

21. F.J. Uribe, E.A. Mason, and J. Kestin, *Physica* **156A**: 467 (1989).

22. *Tablici standartnih i rekomenduemih spravochnih dannih. Annotirovannij ukazatel* (Izdatelstvo standartov, Moskva, 1987).

23. L.R. Fokin, A.N. Kalashnikov, *High Temperature* **38**: N2 (2000).

24. J. Bzowski, J. Kestin, E.A. Mason, and F.J. Uribe, *J. Phys. Chem. Ref. Data* **19**: 1179 (1989).

25. L. Zarkova, *J. Phys. B: At. Mol. Phys.* **30**: 329 (1997).